

**Synthesis of compound 15:**

- (1) HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH (**1**) reacts with N<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et (**2**) in CH<sub>2</sub>Cl<sub>2</sub> (BF<sub>3</sub>·Et<sub>2</sub>O catalyst, 40% yield) to form HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>COOEt (**3**).
- (2) Compound **3** reacts with TsCl, DMAP in pyridine / CH<sub>2</sub>Cl<sub>2</sub> (78% yield) to form TsO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>COOEt (**4**).
- (3) Compound **4** reacts with NaN<sub>3</sub> in DMF (91% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>COOEt (**5**).
- (4) Compound **5** reacts with 1N NaOH in MeOH (98% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>COOH (**6**).
- (5) Compound **6** reacts with MeOOC-CH(Me)-NH-COOMe (**7**) in CH<sub>2</sub>Cl<sub>2</sub> (HOBT, WSCI·HCl catalyst, 80% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>C(=O)-N(CH<sub>2</sub>-COOMe)<sub>2</sub> (**8**).
- (6) Compound **8** reacts with 0.6 N NaOH in MeOH at 0 °C (93% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>C(=O)-N(CH<sub>2</sub>-COOH)<sub>2</sub> (**9**).
- (7) Compound **9** reacts with Fmoc-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH-Fmoc (**10**) in DMF (FDPP, DIPEA catalyst, 40% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>C(=O)-N[CH<sub>2</sub>-C(=O)-N(CH<sub>2</sub>-CONHC(CPh)(OBn))<sub>2</sub>] (**11**).
- (8) Compound **11** undergoes hydrogenation (5% Pd/C, H<sub>2</sub>, MeOH) (80% yield) to remove the benzyl protecting groups.
- (9) The resulting intermediate reacts with HS-(CH<sub>2</sub>)<sub>4</sub>-SH (**13**) in DMF (WSCI·HCl, HOBT catalyst, 59% yield) to form N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>C(=O)-N[CH<sub>2</sub>-C(=O)-N(CH<sub>2</sub>-CONHC(S)-(CH<sub>2</sub>)<sub>4</sub>-S)] (**12**).
- (10) Finally, treatment of **12** with TFA in CH<sub>2</sub>Cl<sub>2</sub> (3 : 1 ratio, 91% yield) removes the Boc protecting group to give the final product, N<sub>3</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>4</sub>CH<sub>2</sub>C(=O)-N[CH<sub>2</sub>-C(=O)-N(CH<sub>2</sub>-CONH<sub>2</sub>)] (**15**).

FIG. 2

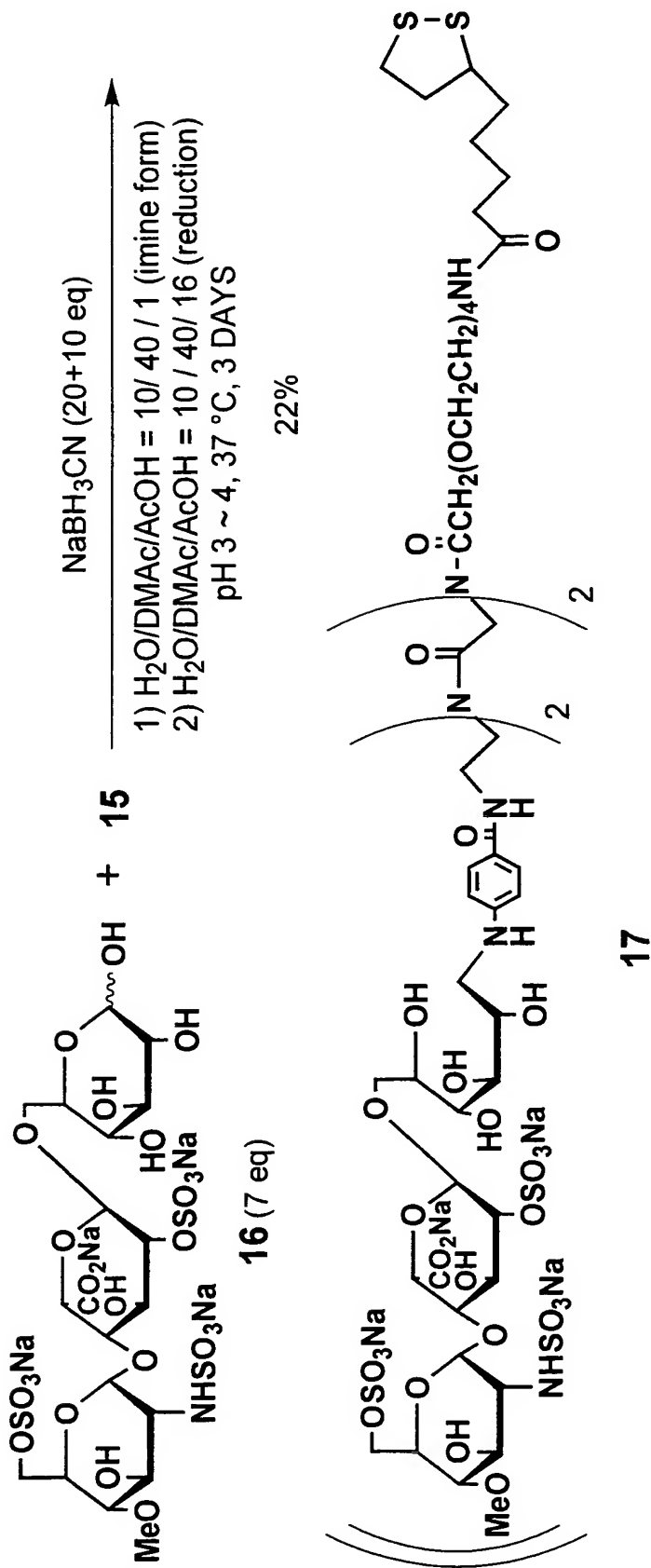


FIG. 3

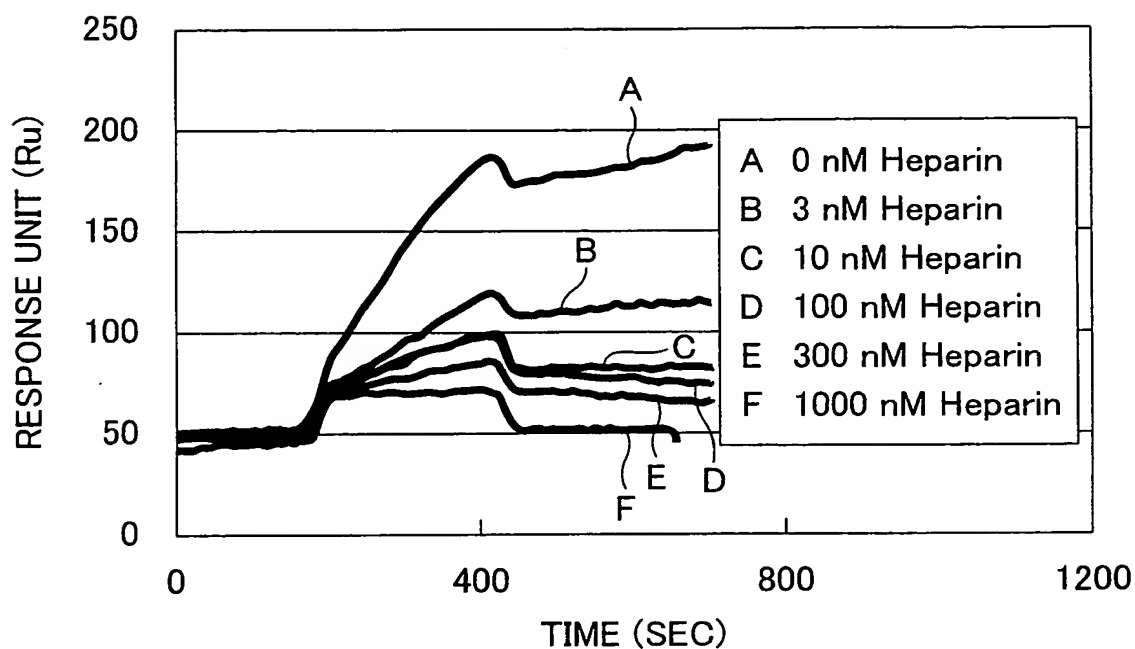
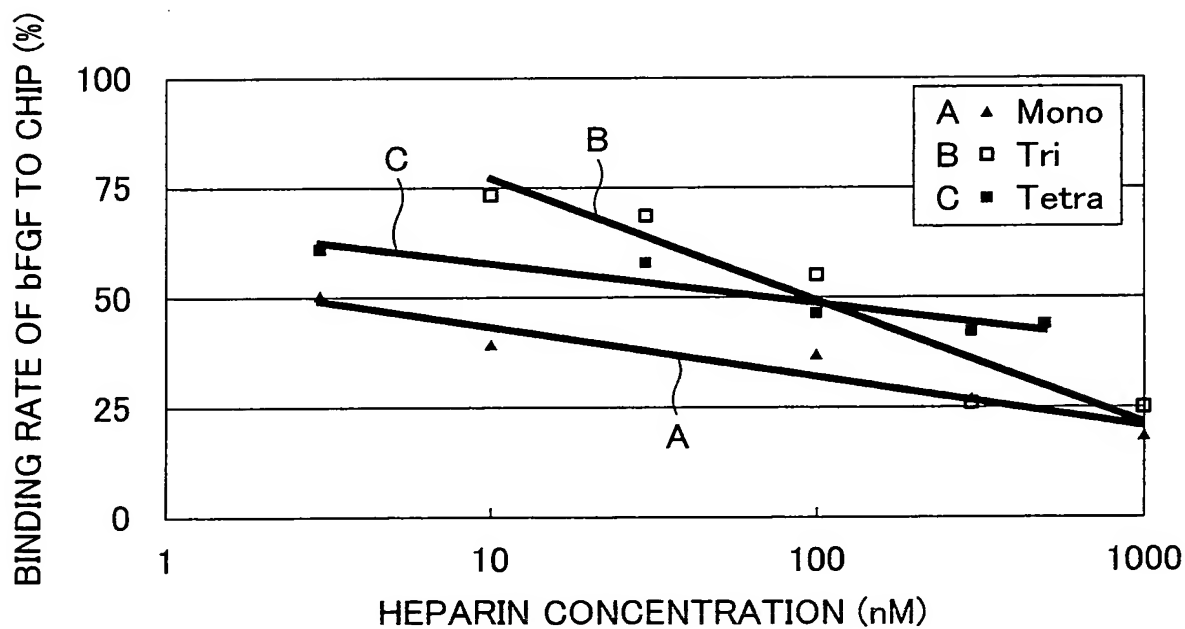


FIG. 4



Mono; Mono-GlcNS6S-IdoA2S-Glc, Tri; Tri-GlcNS6S-IdoA2S-Glc,  
Tetra; Tetra-GlcNS6S-IdoA2S-Glc

FIG. 5 (a)

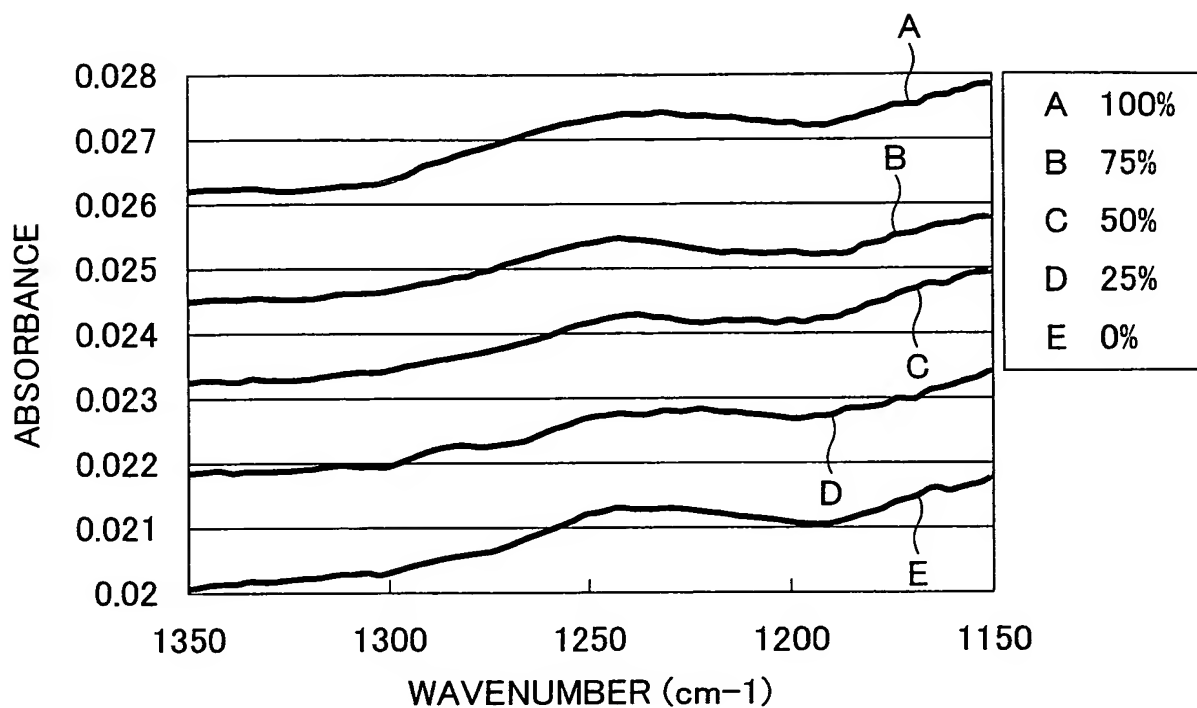


FIG. 5 (b)

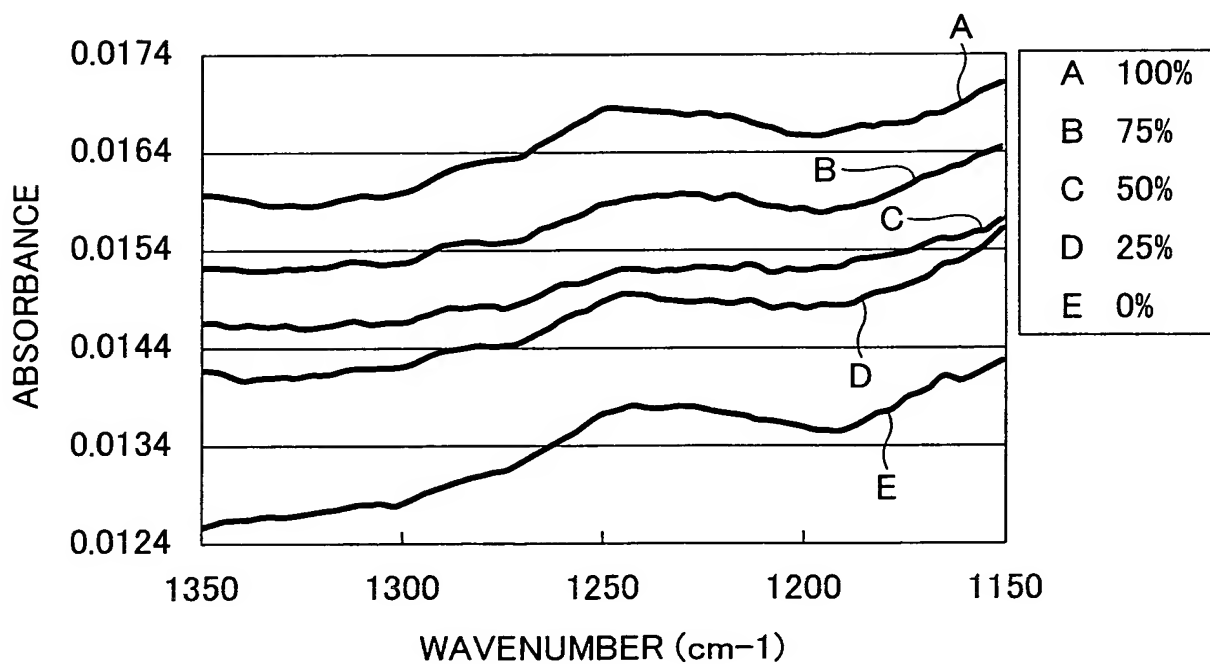


FIG. 6 (a)

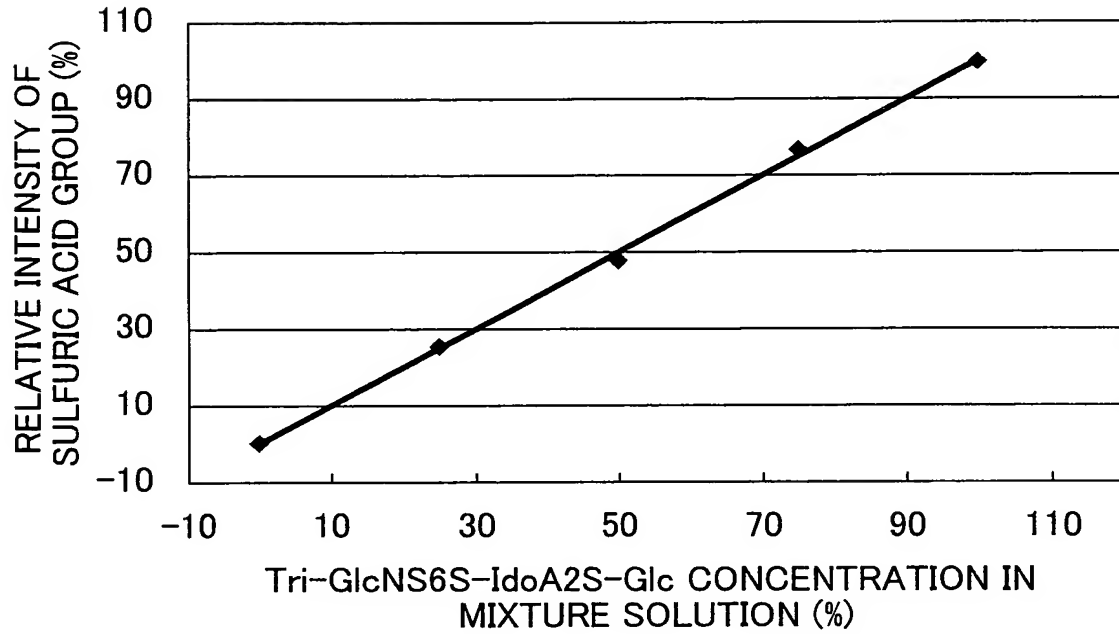


FIG. 6 (b)

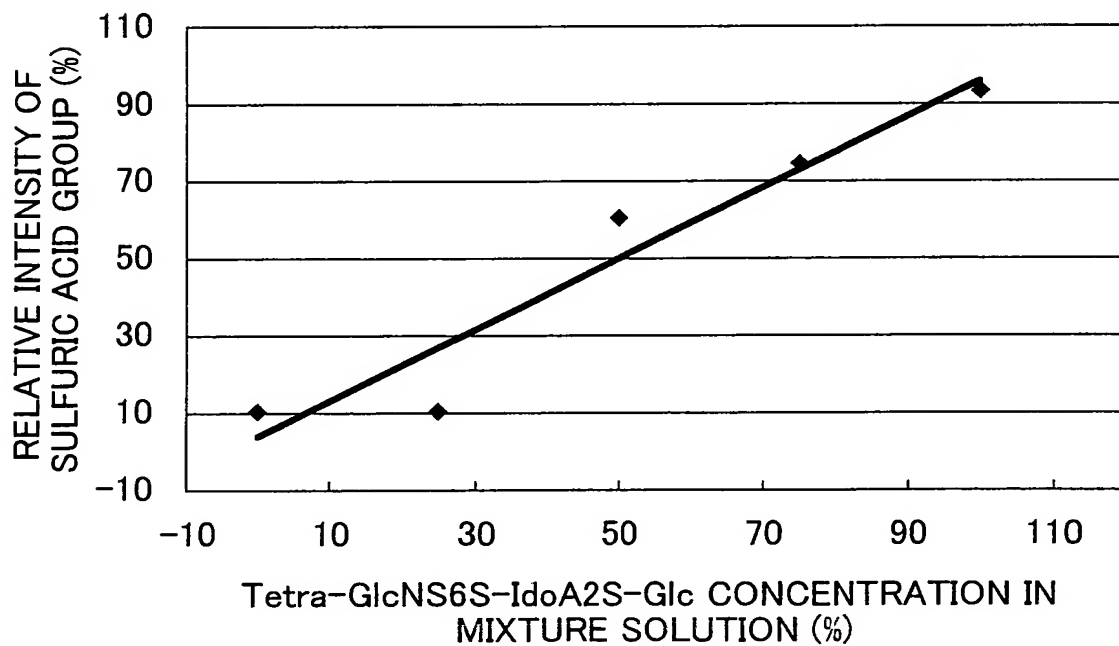


FIG. 7 (a)

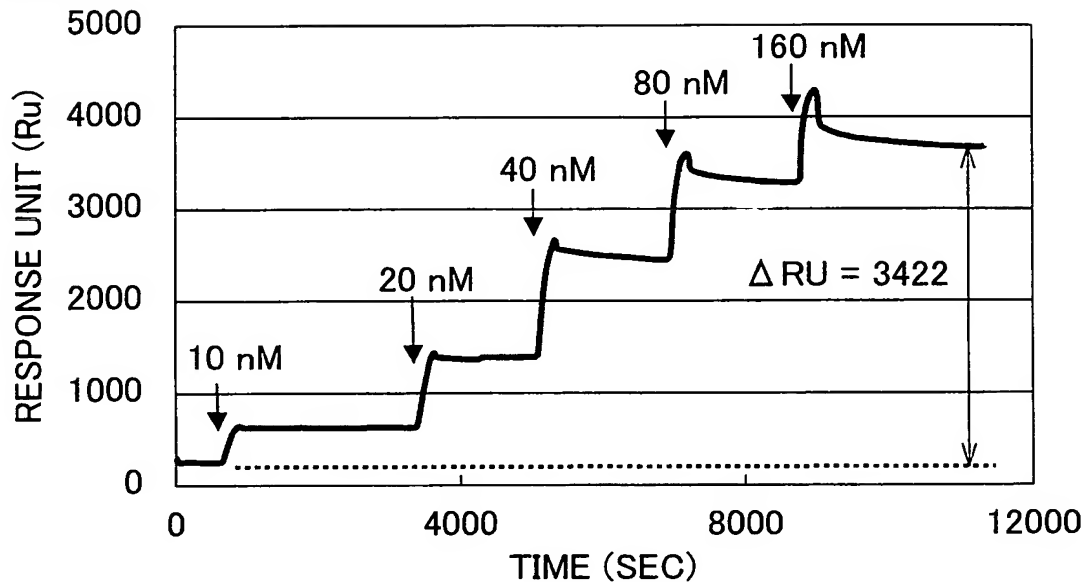


FIG. 7 (b)

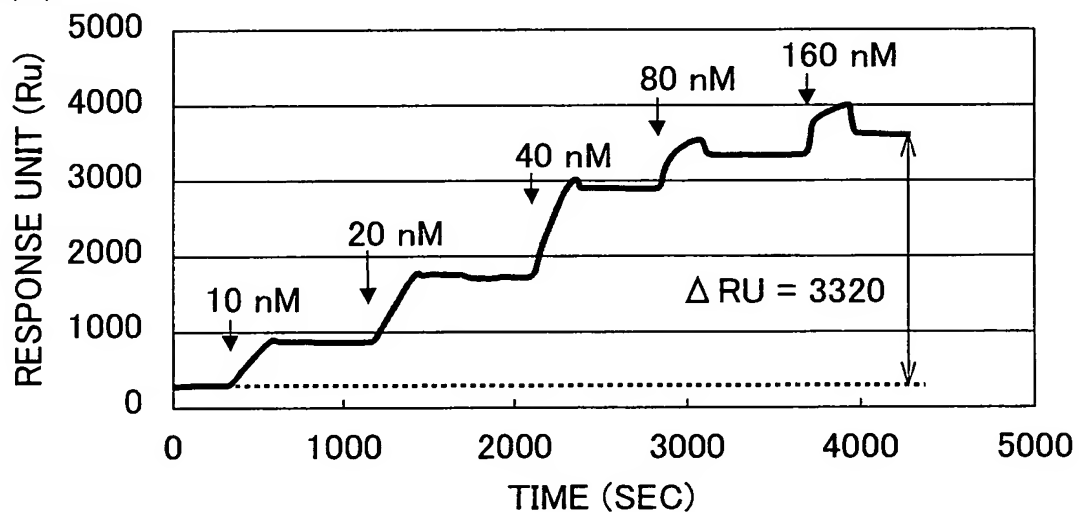


FIG. 7 (c)

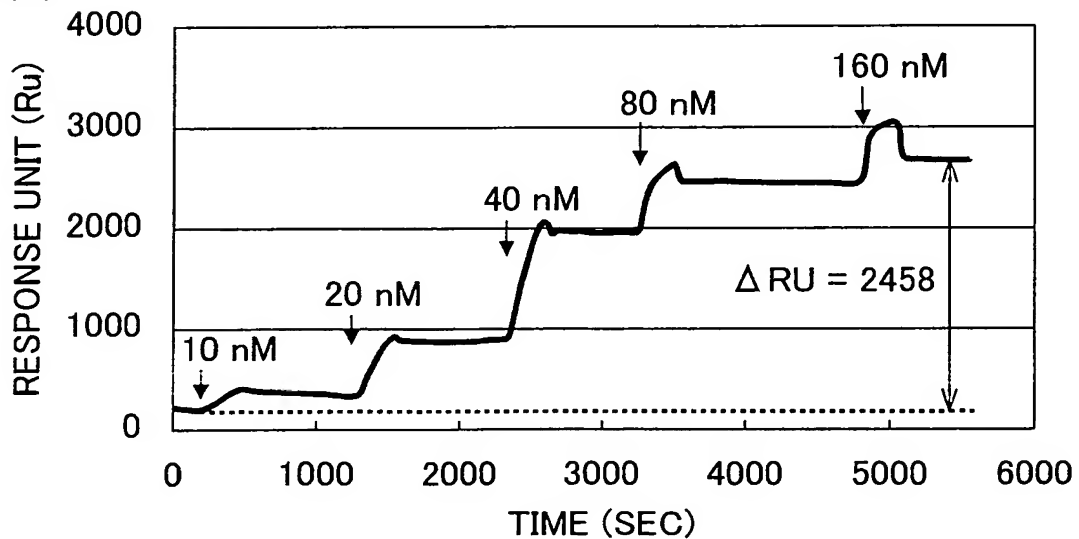


FIG. 8 (a)

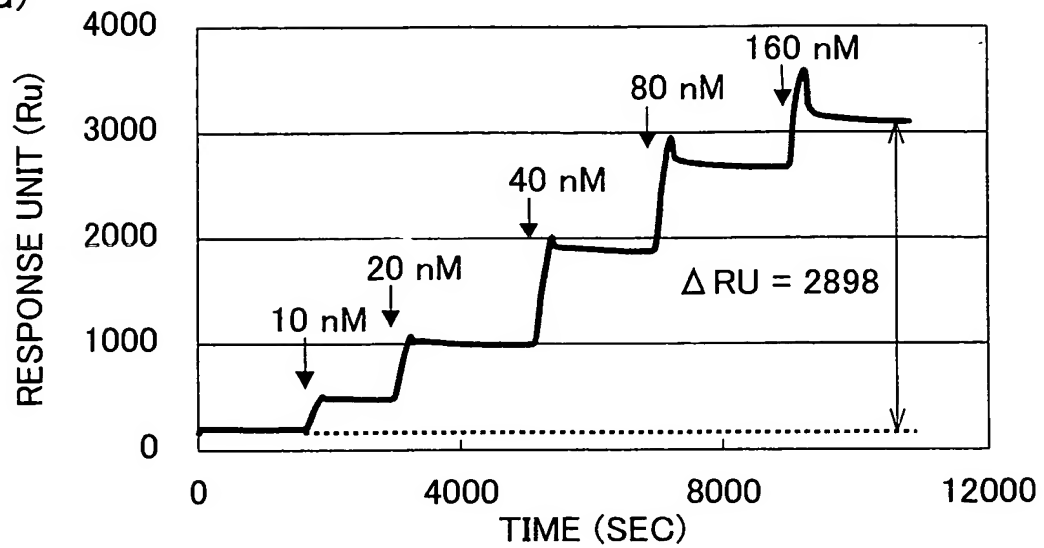


FIG. 8 (b)

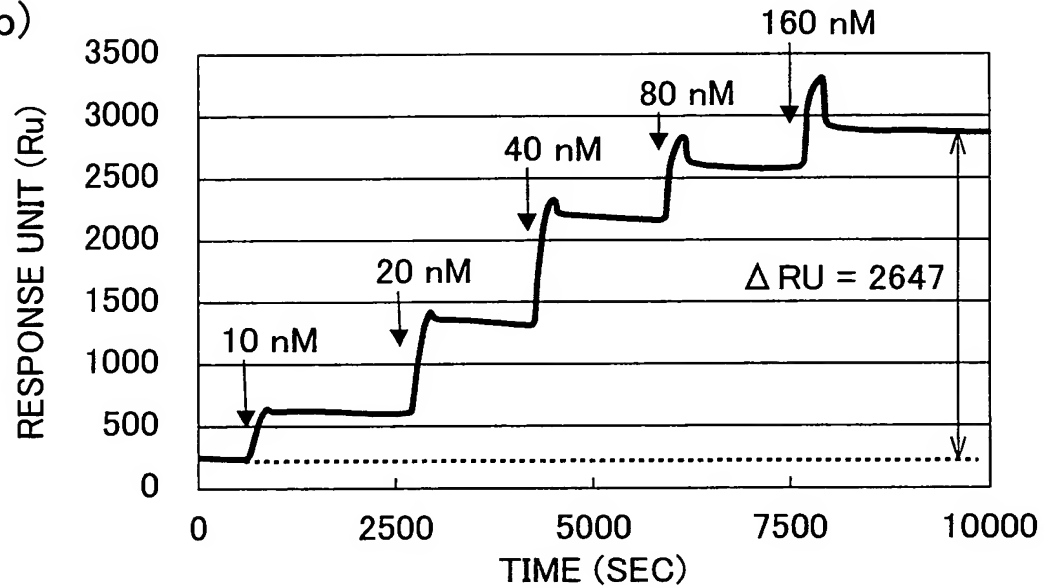


FIG. 8 (c)

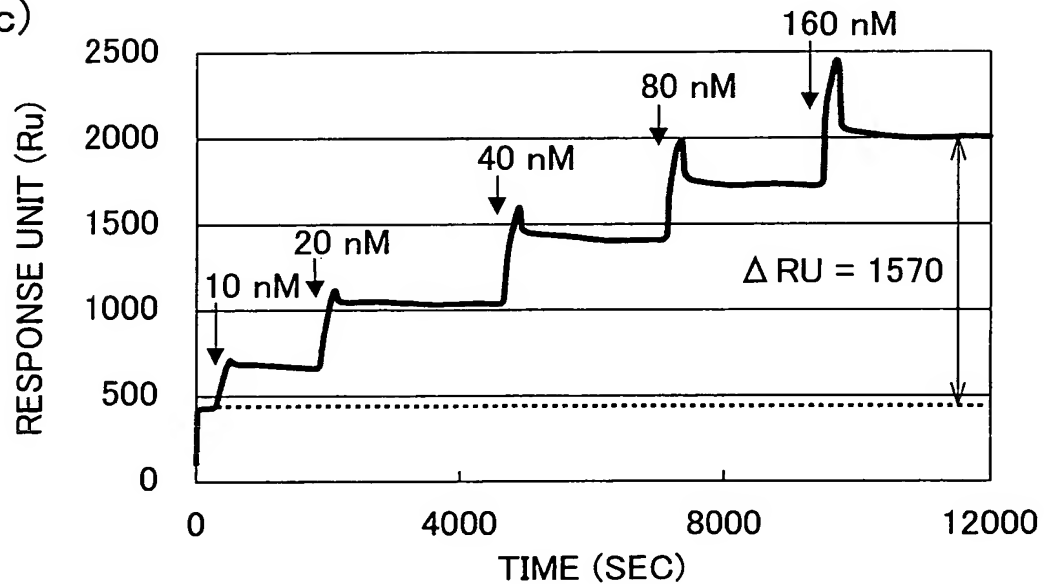


FIG. 9 (a)

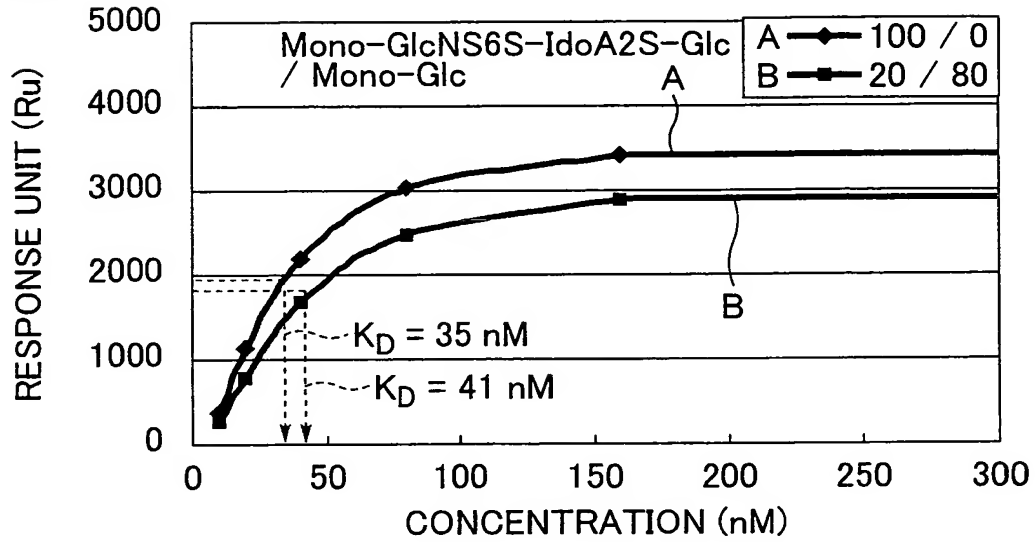


FIG. 9 (b)

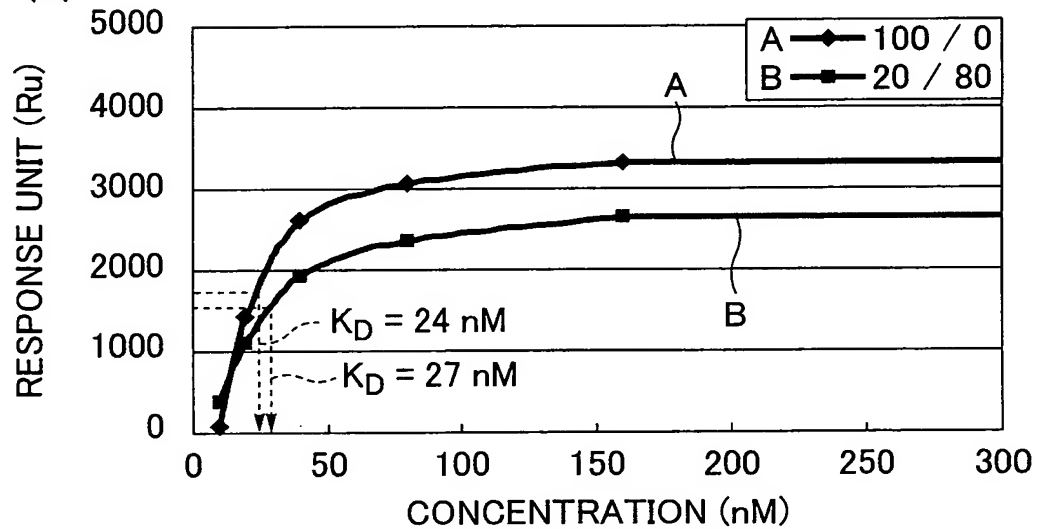


FIG. 9 (c)

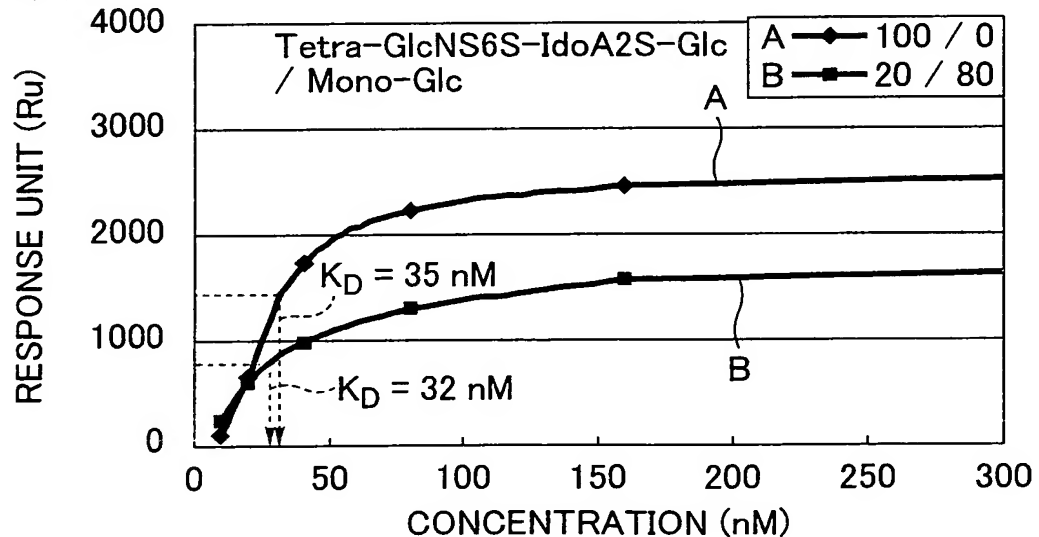




FIG. 10 (a)

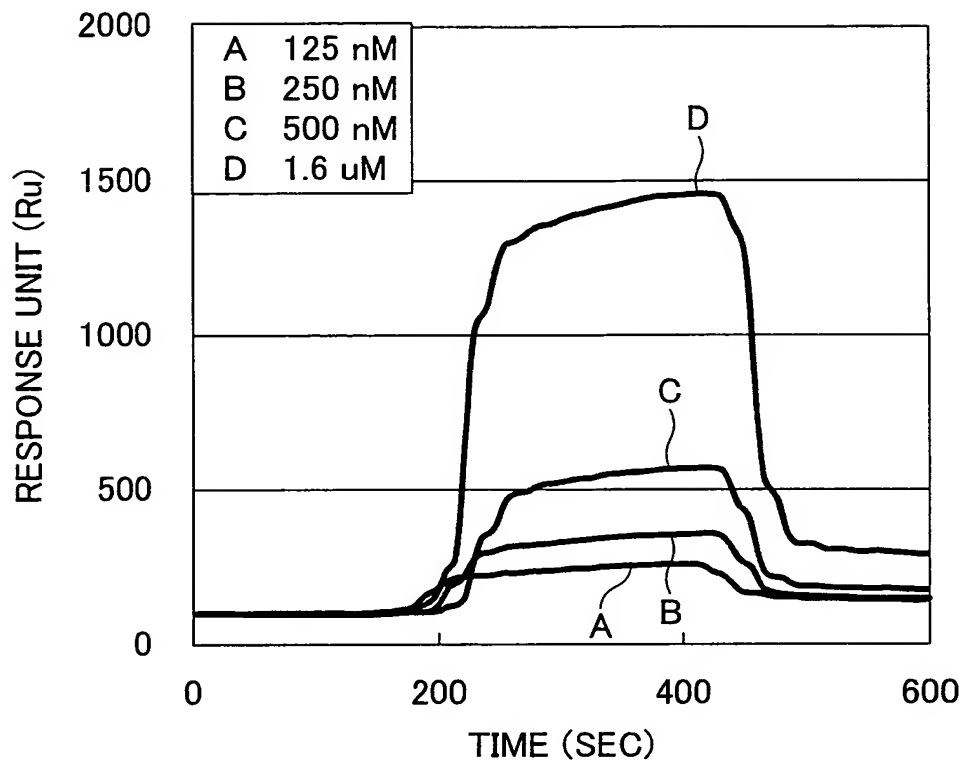


FIG. 10 (b)

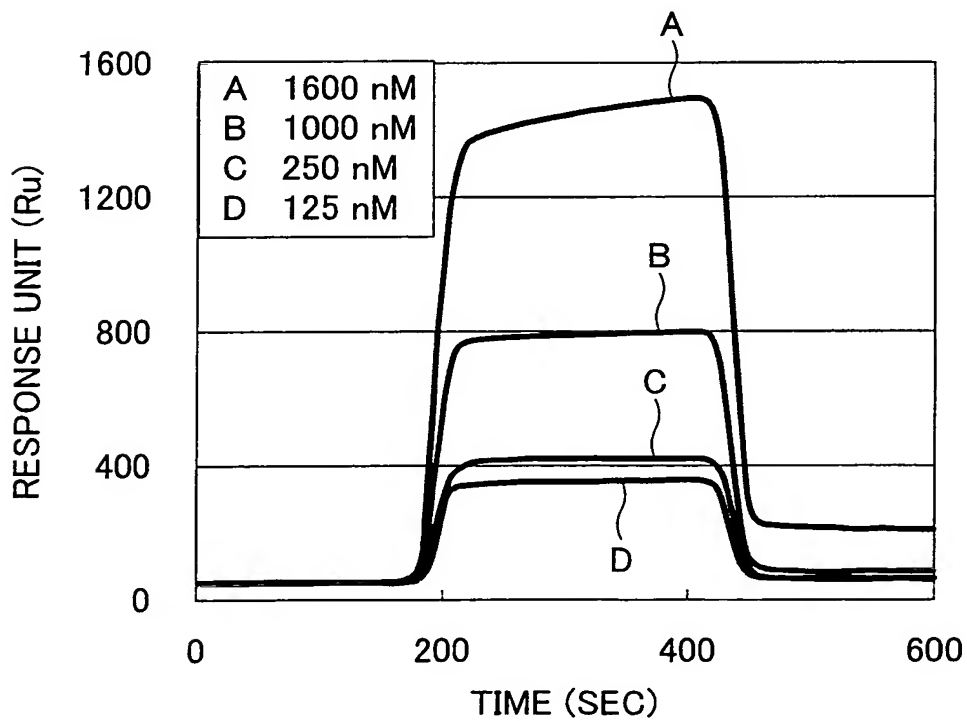


FIG. 11 (a)

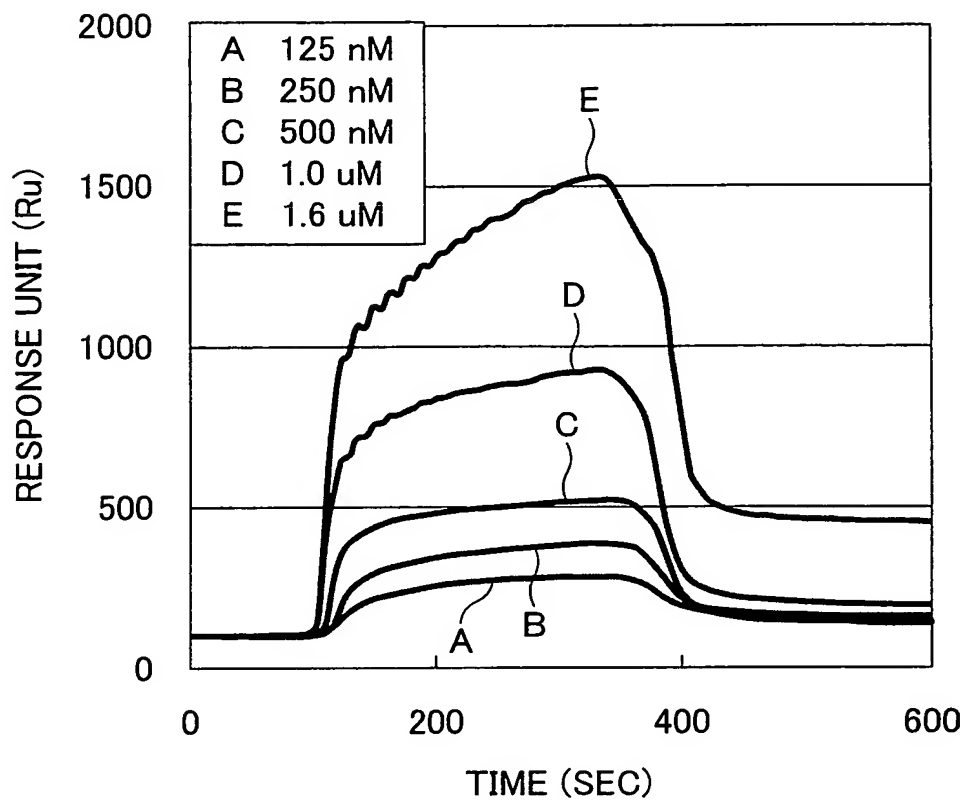


FIG. 11 (b)

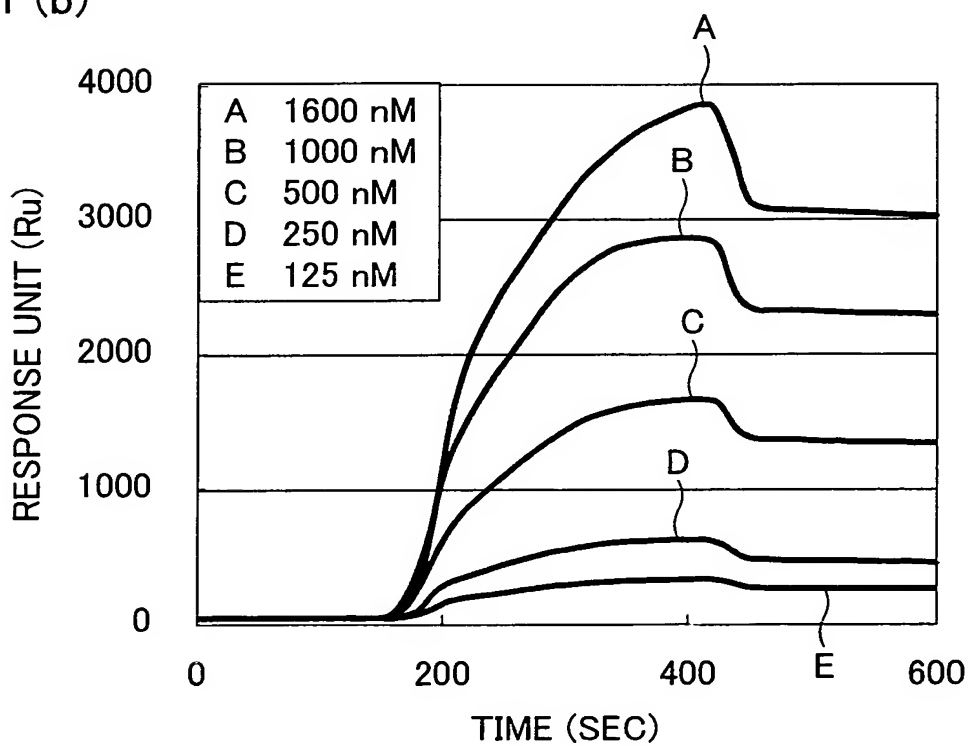


FIG. 12 (a)

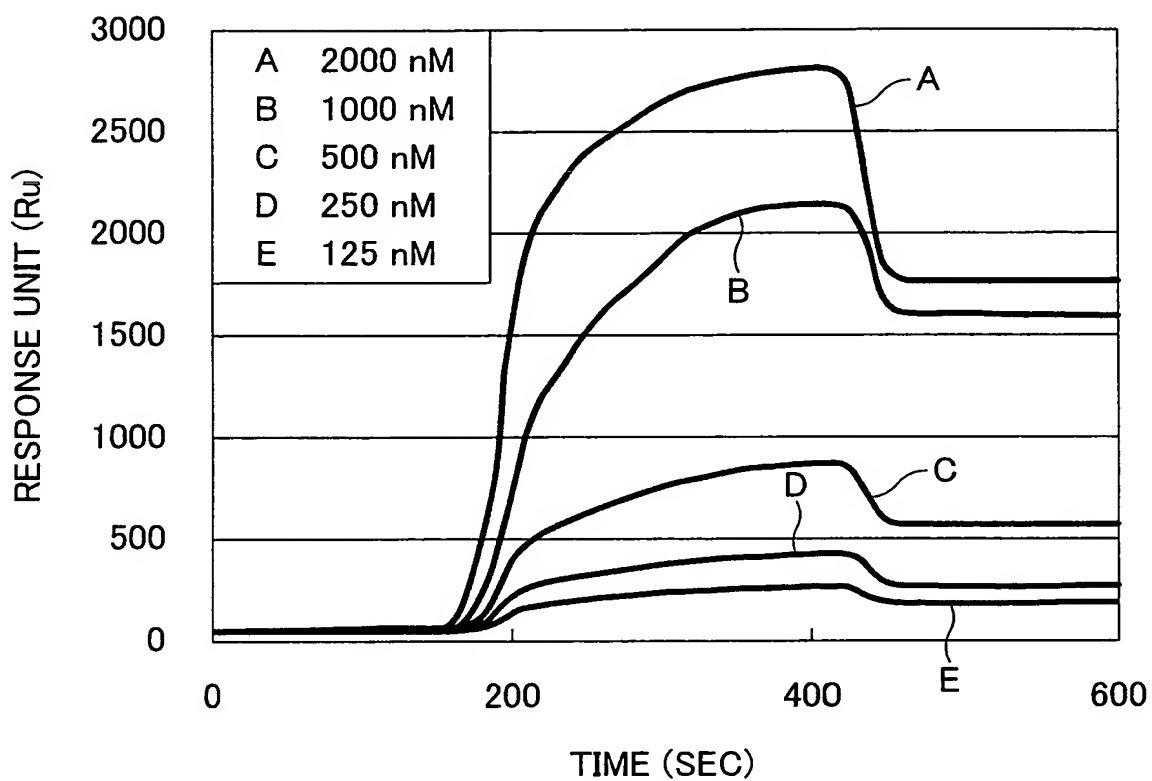


FIG. 12 (b)

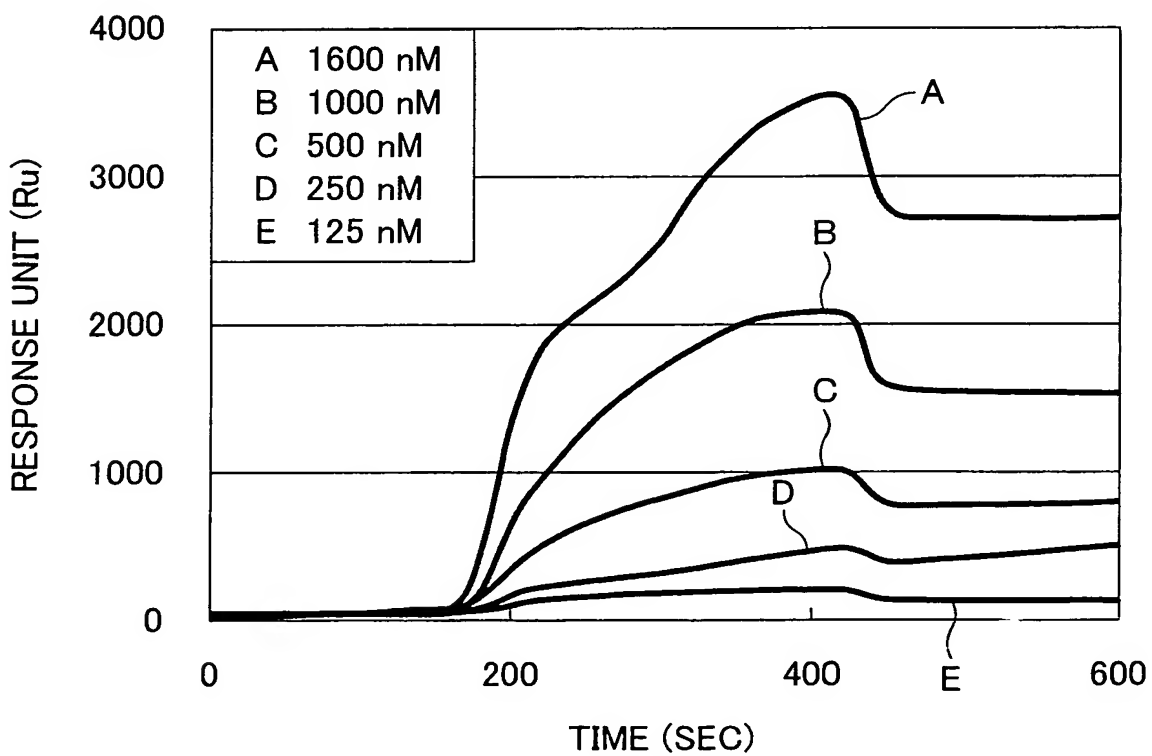


FIG. 13

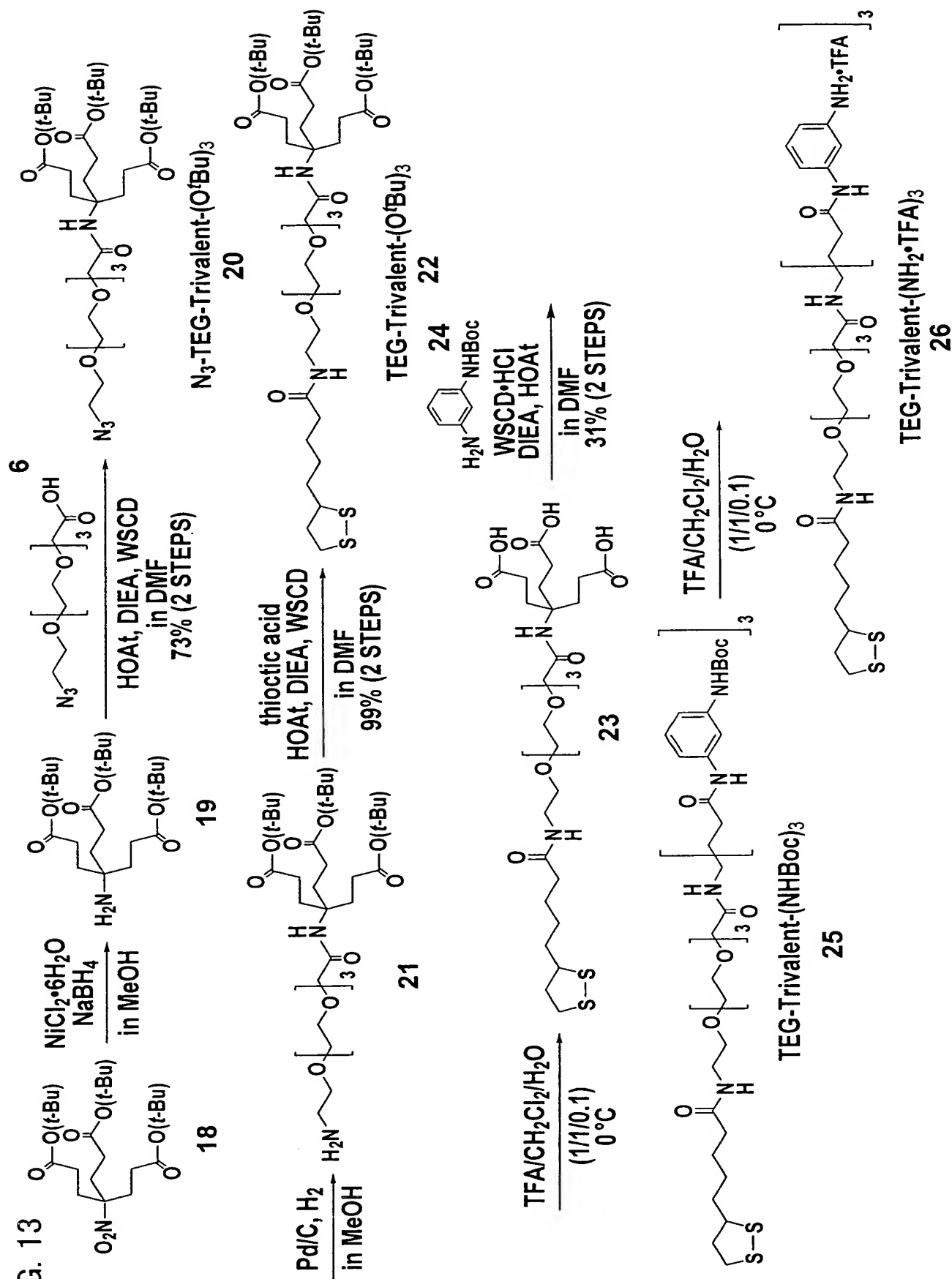


FIG. 14

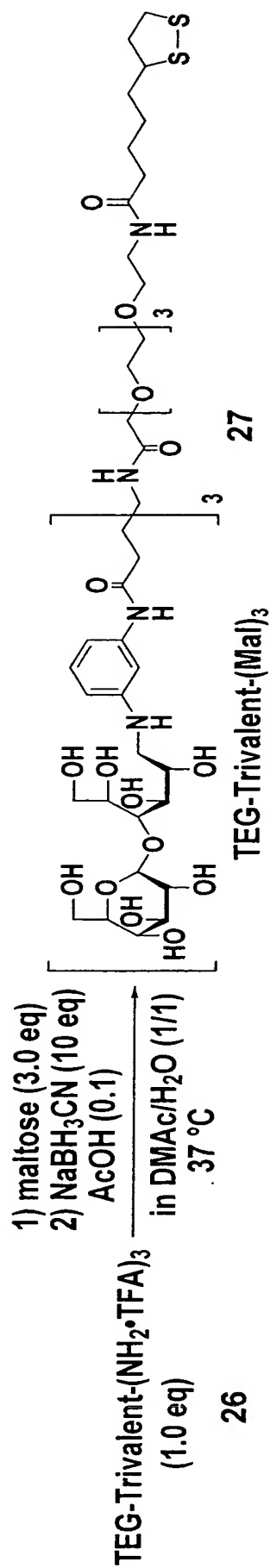


FIG. 15

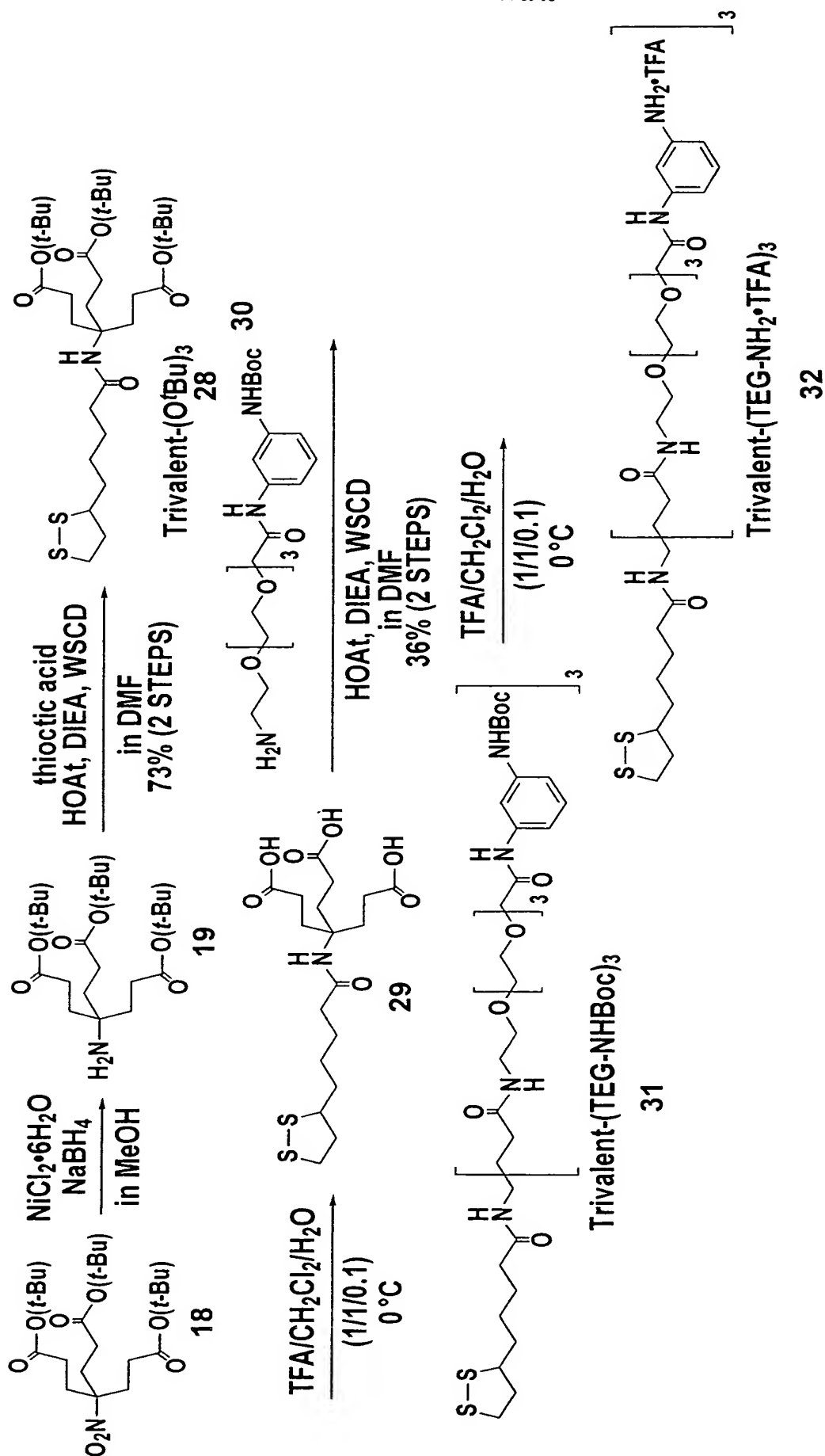


FIG. 16

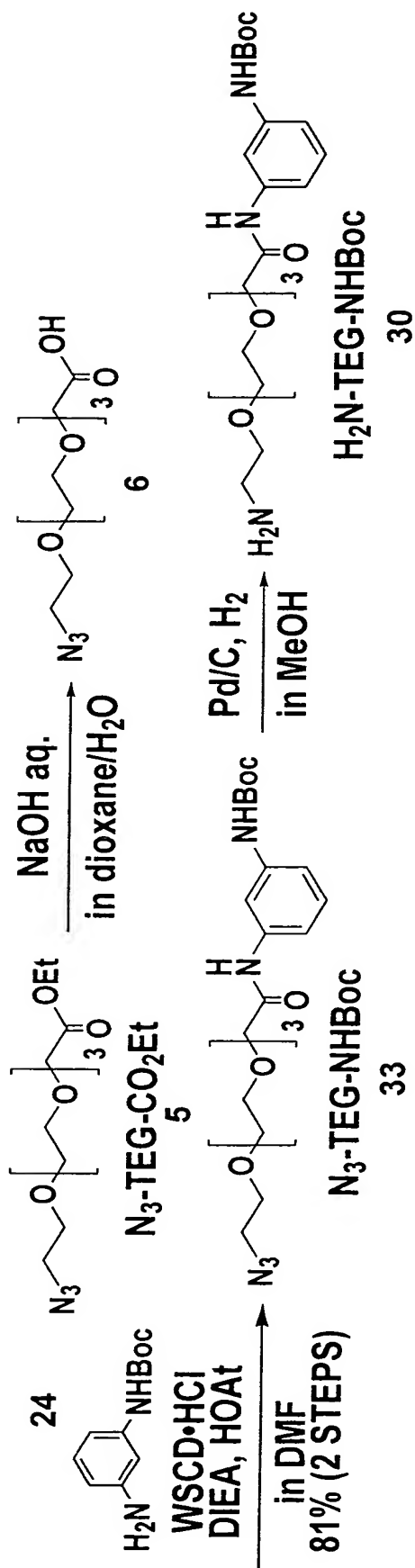


FIG. 17

